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Patent Office

Ottawa, Canada
K1A 0C9

(11) (C) **1,281,339**

(21) 527,255

(22) 1987/01/13

(45) 1991/03/12

(52) 260-679.3

(51) INTL.CL.⁵ C07C-7/20; C07C-11/00

(19) (CA) **CANADIAN PATENT** (12)

(54) Method for Controlling Fouling of Hydrocarbon
Compositions Containing Olefinic Compounds

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(30) (US) U.S.A. 818,583 1986/01/13

(57) 19 Claims

Canada

527255

ABSTRACT OF THE DISCLOSURE

Fouling of equipment used for processing of organic feed streams containing olefinic compounds is controlled by inhibiting polymerization of the olefinic compounds by carrying out the processing in the presence of from about 20 ppb to less than 1000 ppb of a stable free radical, such as a nitroxide.

1 The present invention relates to a method for
2 controlling fouling in equipment for processing and storing
3 hydrocarbon compositions containing unsaturated compounds.
4 More specifically the processing may include, for example,
5 preheating, hydrogenation, fractionation, extraction and the
6 like of hydrocarbon streams to remove, concentrate, or have
7 added thereto the unsaturated hydrocarbons prior to storage
8 or use.

9 The process of recovering olefinic hydrocarbons from
10 gas and liquid cracking operations, the conversion of
11 olefinic and acetylenic compounds by, for example
12 hydrogenation and the separation of the various olefins and
13 acetylenic compounds by distillation or extraction is
14 complicated by the formation of fouling deposits on the heat
15 transfer surfaces of the processing equipment. These
16 deposits decrease the thermal efficiency of the equipment
17 and decrease the separation efficiency of the distillation
18 towers. In addition, operating modifications to reduce the
19 rate of fouling can result in reduced production capacity.
20 The excessive build-up of such deposits can cause plugging
21 in tower plates, transfer tubes, and process lines, which
22 could result in unplanned shutdowns. These deposits are
23 generally thought to result from free radical polymerization
24 induced thermally, by contaminating oxygen or by metal ions.
25 Similar problems are also encountered in olefin recovery
26 operations not connected with thermal cracking, for example,
27 in styrene recovery.



1 Such fouling can be controlled according to the
2 present invention, by the judicious use of an appropriate
3 stable free radical or a suitable precursor that under the
4 process conditions yields the active stable free radical in
5 situ. The fouling is controlled by the action of the stable
6 free radicals in terminating radical polymerization chain
7 reactions in the processing equipment.

8 The use of stable nitroxides and other stable free
9 radicals and precursors thereto are well documented in the
10 patent and open literature as stabilizers for olefinic
11 organic compounds. The prior art teaches that these stable
12 free radicals are useful for the prevention of premature
13 radically induced polymerization of the olefinic monomer
14 during storage and as antioxidants. Typical of this art is
15 US Patent No. 3,747,988 on the stabilization of
16 acrylonitrile; US Pat. No. 3,733,326 disclosing
17 stabilization of vinyl monomers by free radical precursors;
18 US Patent No. 3,488,338 on the stabilization of chloroprene;
19 UK Pat. Spec. 1,127,127 relating to the stabilization of
20 acrylic acid; UK Pat. Spec. 1,218,456 relating to the
21 stabilization of butadiene and the following publications
22 "Inhibition of Radical Polymerization by Nitroxide Mono and
23 Biradicals", L. V. Ruban, et al, Vysokomol. soyed. 8: No. 9,
24 p. 1642 - 1646, 1966; "Iminoxy Radicals as Inhibitors of w -
25 Polymerization of Chloroprene", M. B. Nieman, et al,
26 Vysolomol. soyed, 8: No. 7, p. 1237 - 1239, 1966;
27 "Inhibition of Polymerization of Styrene by a Stable Radical
28 with 4,4'-diethoxy-diphenyl Nitric Oxide", M. D. Goldfein, et

1 al, Vysokomol. soyed. A 16: No. 3, p. 672 - 676, 1974;
2 "Inhibition of Polymerization of Vinyl Monomers by Nitroxide
3 and Iminoxyl Radicals", A. V. Trubnikov, et al., Vysokomol.
4 soyed. A20: No. 11, p. 2448 - 2454, 1978.

5 This art, without exception discloses the use of
6 stable free radicals in excess of 1 ppm and generally well
7 in excess of 10 ppm. Although there is a body of art
8 relating to stable free radicals, these materials are very
9 expensive and usually available or produced only in very
10 limited quantities for research. Hence, the art has
11 consistently taught that which it considered to be the
12 smallest effective amount of stable free radical for
13 stabilization as at least 1 ppm (actually the major portion
14 of the art teaches over 10 times this amount). It has now
15 been surprisingly found that fouling caused by
16 polymerization of olefinic organic compounds can be
17 effectively controlled with substantially less than the 1
18 ppm of stable free radical taught by the art as the lowest
19 level. Although the stable nitroxide free radical compounds
20 are currently, principally of academic interest there is an
21 abundance of art on their preparation, for example, the
22 following US Pat. No.'s, 3,494,930; 3,966,711; 3,704,233;
23 3,334,103; 3,253,015; 3,372,182; 3,502,692; 3,422,144;
24 3,163,677 and 3,873,564.

25 It is an advantage of the present invention that
26 fouling in processing equipment for hydrocarbon streams
27 containing olefinic organic compounds, may be controlled by
28 the present invention. It is a feature of the present
29 invention that stable free radicals, which have been

1 laboratory curiosities until now because of their high cost,
2 can now be beneficially employed commercially for
3 stabilization. These and other advantages and features will
4 become apparent from the following description.

5 Generally the present invention relates to the
6 discovery that polymerization of unsaturated organic
7 compounds (olefinic or acetylenic unsaturation) contained in
8 organic feed streams can be controlled and inhibited during
9 processing of the streams by incorporating from 20 to less
10 than 1000 ppb (parts per billion by weight), preferably to
11 900 ppb, of a stable free radical into the stream, based on
12 the total stream being processed. Briefly, the present
13 invention is a method for inhibiting polymerization of
14 unsaturated compounds in organic feed streams during
15 processing of said feed streams comprising having present
16 from 20 to less than 1000 ppb, preferably 50 to 900 ppb and
17 more preferably less than 700 ppb by weight of a stable free
18 radical, based on the total weight of said feed stream,
19 thereby controlling fouling of processing equipment.

20 The feed streams may be hydrocarbons or unsaturated
21 compounds and may contain other substituents in addition to
22 hydrogen and carbon. Similarly the entire feed stream may be
23 comprised of substituted hydrocarbons. The unsaturated
24 compounds may comprise from 1 to 100% of the feed stream.

25 The processing may include distillation, extraction,
26 heating, vaporizing and hydrotreating of the feed stream,
27 wherein the unsaturated compound is removed, concentrated or
28 reacted, as in hydrotreating, or some other component of the
29 feed stream is removed, concentrated or reacted. The amount
30 of stable free radical used in the process is quite small,

1 hence product streams, e.g., olefins, produced according to
2 the present method can be utilized for polymerization by the
3 addition of conventional amounts of polymerization catalyst
4 under polymerization conditions, which will overcome the
5 inhibiting effect of any stable free radical remaining in
6 the product. In distillation the stable free radical may be
7 selected to be higher boiling than the overhead, hence it
8 will remain bottoms. Thus, for example, in ethylene
9 recovery there will be no stable free radical in the
10 ethylene overhead product to interfere with subsequent
11 polymerization. The present method excludes any process
12 carried out for the purpose of polymerizing the unsaturated
13 compounds, particularly in the presence of effective amounts
14 of polymerization catalyst. In a particular application it
15 has been found that the spontaneous and unexplained
16 formation of "popcorn polymer" in distillation equipment in
17 the vapor portion of the equipment used to separate and
18 recover some olefins, e.g., butadiene and styrene overhead,
19 is inhibited according to the present invention.

20 The products resulting from the present method of
21 processing may also be stabilized from unsaturated
22 hydrocarbon polymerization provided the appropriate amount
23 of the stable free radical, as recited above for the feed
24 stream processing, is present in the product.

25 The term "stable free radical" as used herein shall
26 mean a free radical that can be prepared by conventional
27 chemical methods and will exist long enough to be used in a
28 subsequent chemical reaction or examined in a static system
29 by normal methods of spectroscopy. Generally the stable

1 free radicals of the present invention have a half life of
2 at least one (1) year. The term "half life" as used herein
3 means that period of time at the end of which one-half of
4 the radicals, existing at the beginning of said time period
5 are still in existence. The term "stable free radical"
6 shall also be understood to include the precursor to a
7 stable free radical from which the stable free radical may
8 be produced in situ.

9 BRIEF DESCRIPTION OF THE DRAWING

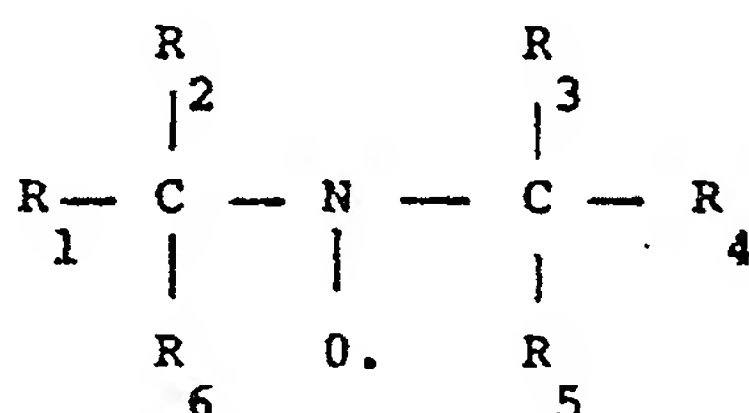
10 Fig. 1 is a plot showing the results from a process
11 carried out according to the present invention and from the
12 same process carried out in accordance with prior practice.
13 The scale of the wall resistance is increased by a factor of
14 10^4 for the drawing.

15 Any stable free radical (or precursor thereof under
16 conditions which produce the stable free radical in situ) as
17 defined may be used in the present invention. The stable
18 free radicals suitable for use in this invention may be
19 selected from, but are not limited to, the following groups
20 of chemicals: nitroxides (e.g., di-tert-butyl nitroxide),
21 hindered phenoxys (e.g., galvinoxyl), hydrazyls (e.g.,
22 diphenylpicrylhydrazyl), and stabilized hydrocarbon radicals
23 (e.g., triphenylmethyl), as well as polyradicals, preferably
24 biradicals of these types. In addition, certain precursors
25 that produce stable free radicals in situ may be selected
26 from the following groups: nitrones, nitrosos, thioketones,
27 benzoquinones, and hydroxylamines.

28 These stable free radicals exist over a wide range
29 of temperatures up to 260° C. A limiting factor in

1 their use is the temperature of the processing wherein they
 2 are employed. Specifically the present method applies to
 3 processing carried on at temperatures at which said stable
 4 free radical exists. Generally such processing is conducted
 5 at less than 260° C eg, 0 to 260°C . Pressure has not
 6 been seen to be significant to the present method, hence,
 7 atmospheric, sub or superatmospheric conditions may be
 8 employed. A preferred stable free radical for use in this
 9 invention is a nitroxide having the formula:

10



11 wherein R₁, R₂, R₃ and R₄ are alkyl groups or heteroatom substituted
 12 alkyl groups and R₅ and R₆ are such that no hydrogen is bound to the
 13 remaining valences on the carbon atoms bound to the nitrogen.

14 The alkyl (or heteroatom substituted) groups
 15 R₁-R₄ may be the same or different, and preferably
 16 contain 1 to 15 carbon atoms. Preferably R₁-R₄ are
 17 methyl, ethyl, or propyl groups.

18 The heteroatom substituents may include halogen, oxygen,
 19 sulfur and nitrogen.

20 The remaining valences (R₅ and R₆) in the
 21 formula above may be satisfied by any atom or group except
 22 hydrogen which can bond covalently to carbon, although some
 23 groups may reduce the stabilizing power of the nitroxide
 24 structure and are undesirable. Preferably R₅ and R₆

1 are halogen, cyano, -COOR wherein R is alkyl or aryl,
2 -CONH₂, -S-C₆H₅, -S-COCH₃, -OCOC₂H₅,
3 carbonyl, alkenyl where the double bond is not conjugated
4 with the nitroxide moiety or alkyl of 1 to 15 carbon atoms,
5 R₅ and R₆ may also form a ring of 4 or 5 carbon
6 atoms and up to two heteroatoms, such as O, N or S by R₅
7 and R₆ together. Examples of suitable compounds having
8 the structure above and in which R₅ and R₆ form part
9 of the ring are those containing a carbonyl group such as the
10 pyrrolidin-1-oxys, piperidinyl-1-oxys, or pyrrolin-1-oxys and the
11 morpholines and piperazines. Particular examples wherein the
12 R₅ and R₆ above form part of a ring are
13 4-hydroxy-2,2,6,6-tetramethyl-piperidino-1-oxy,
14 2,2,6,6-tetramethyl-piperidino-1-oxy,
15 4-oxo-2,2,6,6-tetramethyl-piperidino-1-oxy and
16 pyrrolin-1-oxyl. Suitable R₅ and R₆ groups are methyl, ethyl and
17 propyl groups. R₁, R₂, R₃, R₄, R₅ and R₆ may each be, for example,
18 methyl, ethyl or propyl. A specific example of a suitable compound
19 where R₁ - R₆ are alkyl groups is di-tert-butyl nitroxide. The
20 preferred carbonyl containing nitroxides are those wherein the R₅ and
21 R₆ form a ring structure with the nitrogen, preferably a six member
22 ring, for example, 4-oxo-2,2,6,6-tetramethylpiperidino-1-oxy.
23 In one embodiment the nitroxide is present in the feed stream at a
24 concentration of from 20 to 100 ppb.

25 The feed streams are organic, preferably
26 hydrocarbons containing hydrocarbon olefinic and/or
27 acetylenic compounds. The unsaturated compounds may be pure
28 hydrocarbons or organic unsaturated compounds or mixtures
29 thereof.

30 The processing to which the present invention is

1 directed includes distillation, extraction, extractive
2 distillation, countercurrent extraction, hydrotreating,
3 hydrofining, thermal treatments and the like, and the
4 preheating prior to such processing. Those processes which
5 are intended to produce polymer by free radical initiation,
6 coordination type catalyst, or otherwise are excluded;
7 however, the presence of the present stable free radicals in
8 feeds used for polymerizations as a result of prior
9 processing according to the present invention is not
10 precluded, since the catalytic concentrations of
11 polymerization catalyst readily overwhelm the parts per
12 billion of stable free radical residual from the present
13 invention.

14 The olefinic compounds include hydrocarbon monomers
15 generally having two to 20 carbon atoms such as ethylene,
16 propylene, butene-1, isobutene, pentene, hexene, octene,
17 dodecene, butadiene, isoprene, hexadiene and the like; vinyl
18 monomers such as vinyl chloride, vinyl acetate, vinylidene
19 chloride, ethyl vinyl ketone, chloroprene, styrene,
20 divinylbenzene, vinyl pyridiene, chlorostyrenes, esters of
21 acrylic acid and methacrylic acid, acrylamide,
22 acrylonitrile, methacrylonitrile, acrolein, methacrolein and
23 the like. Acetylenic compounds include, for example vinyl
24 acetylene, methyl acetylene and the like. The unsaturated
25 compounds may also include higher molecular weight compounds
26 found in crude oil and crude oil distillates and residua
27 which are normally identified by their solubility
28 characteristics, such as asphaltenes and maltenes.

29 The processing carried out according to the present

1 invention results in a wide variety of liquid (under the
2 appropriate conditions of pressure) compositions containing
3 the stable free radical. Some of these compositions may
4 contain olefinic materials for use in polymerizations or
5 otherwise or for other end uses or processing.

6 There may be present in the present method in
7 addition to the stable free radical as described, other
8 additives such as antioxidants, anti-foaming agents, color
9 stabilizers and the like.

10 A preferred mode of operation for the present
11 invention is the fractionation of an organic feed stream to
12 recover olefinic compound contained therein, e.g., low
13 molecular weight olefinic hydrocarbons, such as ethylene, propylene,
14 butenes, butadiene and mixtures thereof from a bottoms liquid
15 containing other C₂ to C₇ olefinic hydrocarbons thereby inhibiting
16 polymerization and controlling fouling in the distillation
17 towers, reboilers and associated equipment, a particular
18 example of such a separation being the removal of ethylene
19 from a low boiling hydrocarbon cut, e.g., a C₇ cut.

20 The stable free radical may be for example a nitroxide having a
21 boiling point above that of the separated olefinic compound.

22 Past experience with the operation of a deethanizer unit has
23 shown that polymer build up resulting in fouling of the
24 distillation tower walls and plugging of reboiler tubes
25 required a shut down of the reboiler about every thirty days
26 for removal of the polymer. The primary detriment from the
27 fouling is the reduction in the heat transfer in the
28 reboiler of the tower. In order to avoid fouling, milder
29 conditions are frequently used, requiring recycle of the

1 distillate products, lower compressor efficiency and higher
2 refrigeration costs. In order to maintain a given level of
3 operation at a given pressure the heat input to the tower
4 must be increased as the polymer builds up. The same
5 processing carried out according to the present method
6 results in low levels of fouling. This is shown by Fig. 1
7 which is presented by way of illustration only of certain
8 aspects of the invention, and which shows what happened
9 where a deethanizer was operated without a stable free
10 radical and had an increase in wall resistance to the point
11 that it was necessary to shut down for cleaning at around 36
12 days (Base Run). Wall resistance is the resistance of a
13 wall to the flow of thermal energy from one side to the
14 other. In this instance, wall resistance refers to the
15 transfer of heat across the walls of tubes in a reboiler.
16 In this regard it is qualitatively the inverse of the more
17 conventionally used heat transfer coefficient. The wall
18 resistance values used in Fig. 1 are derived from heat
19 transfer coefficient values and appropriate corrections for
20 steam rates, process rates, condensate levels, and other
21 similar parameters affecting the operation of the trial unit
22 expressed as Hour, feet squared, degrees fahrenheit per BTU
23 ($\text{hr ft}^2 \text{ } ^\circ\text{F}/\text{BTU} = 4.9 \times 10^{-5} \text{ h.m}^2 \text{ } ^\circ\text{C.J}^{-1}$).

24 Wall resistance can be used as an indicator of
25 fouling because of the fact that as fouling material is
26 deposited on the heat transfer surface it forms an
27 additional layer of resistance that must be overcome.
28 Because the wall resistance is calculated from the
29 temperature difference of the fluids on each side of the

1 wall, this layer of fouling causes an increase in the
2 calculated wall resistance. Thus an increase in the wall
3 resistance is indicative of an increase in fouling.

4 Brief excursions, such as those seen in Fig. 1, may
5 arise from sudden changes in process conditions that are not
6 accounted in the wall resistance calculations. Fouling is
7 indicated by the long-term trend of the wall resistance.

8 The same equipment and process carried out in the
9 presence of less than 500 ppb
10 4-hydroxy-2,2,6,6-tetramethylpiperindinyloxy (HTMPO) based
11 on bottoms production rate showed almost no polymer build up
12 as evidenced by the low wall resistance during the same
13 period and has continued to operate without fouling for over
14 100 days.

15 The following Example is now given, by way of illustration only:

16 Example:

17 To further demonstrate the effectiveness of the
18 present invention two stable free radicals were tested
19 against several commercial anti-fouling additives on an
20 apparatus designed to simulate fouling in a dynamic manner.
21 This test is designed to detect the formation of insoluble
22 polymer by passing the test fluid through an orifice. The
23 fouling of a particular fluid is detected by recording the
24 change in the pressure across an appropriately sized orifice
25 through which the test fluid is passed. The deposition of
26 fouling material on the surface of the orifice restricts the
27 flow path resulting in an increase in the pressure drop over
28 the length of the orifice.

1 The analysis of the effects of additives is
 2 accomplished by comparing the times required for the
 3 pressure difference across the orifice to reach a
 4 predetermined value for a fluid containing the additive and
 5 the fluid alone. The variation in the characteristics of
 6 the fluids and the configuration of the analyzer compared to
 7 that of a full-scale plant precludes an extrapolation of the
 8 results from laboratory to plant. However, the results are
 9 useful in identifying additives that inhibit fouling of the
 10 test fluids and in ranking the effectiveness of several
 11 additives in inhibiting fouling.

12 The formation of polymer is detected by observing
 13 the change in the pressure drop across the restriction. Run
 14 length is defined as the time required for the pressure to
 15 increase by a predetermined amount. Table 1 shows the
 16 results of tests on a number of compounds and formulations
 17 which are active in inhibiting the formation of the
 18 polymeric fouling material.

TABLE 1

| 20 <u>ADDITIVE</u> | <u>RUN LENGTH (MINUTES)</u> |
|---|-----------------------------|
| 21 Blank Feed (50% butadiene) | 5 - 6 |
| 22 <u>Commercial Additives (10,000 ppb - active concentration)</u> | |
| 2,6-Di-tert-butyl-4-methylphenol (BHT) | 7.3 |
| 4-Methoxyphenol (MEHQ) | 7.4 |
| Nonylphenol-formaldehyde resin (50% active) | 9.1 |
| Nonylphenol-formaldehyde resin-Trisnonyl- phenylphosphite | 11.5 |
| Formulation 7 * | 8.3 |
| Formulation 10 * | 9.9 |
| <u>Invention Additives 100 ppb</u> | |
| 4-Hydroxy-2,2,6,6-tetramethyl- piperidinyloxy (HTMPO) | 8.6 |
| Di-tert-butyl nitroxide | 13.6 |
| * Proprietary blend of dispersant, antioxidant and metal chelant | |

1 As can be seen from the length of runs in TABLE 1
2 the stable free radical will obtain substantially the same
3 result as 100 times as much of the commercial additives.

4 Table 2 summarizes the results of treating a similar
5 feed with HTPMO.

TABLE 2

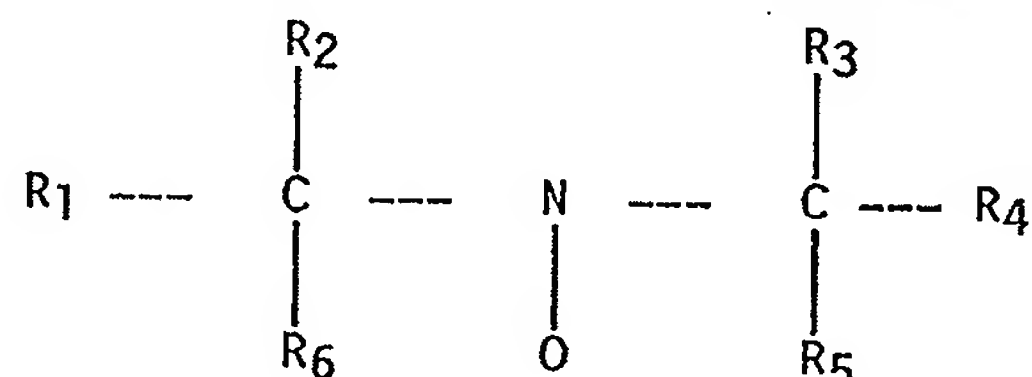
| <u>ADDITIVE (CONCENTRATION)</u> | <u>RUN LENGTH MINUTES)</u> |
|---------------------------------|----------------------------|
| Blank feed (50% butadiene) | 13.1 |
| Blank feed (50% butadiene) | 13.8 |
| HTMPO (100 ppb) | 72 |
| HTMPO (2000 ppb) | 92 |

7 This example demonstrates that a twenty fold
8 increase in stable free radical produces only a small
9 incremental increase in fouling inhibition.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. In a process wherein an organic feed stream containing one or more unsaturated olefinic hydrocarbons is separated into an overhead stream of an olefinic compound selected from ethylene, propylene, butenes, butadiene and mixtures thereof, and a bottoms liquid containing other unsaturated olefinic hydrocarbon liquids including one or more C_2 to C_7 hydrocarbons, the improvement wherein an effective amount of a stable free radical is introduced into the feed stream to inhibit fouling by the bottoms liquid, said stable free radical being a nitroxide having a boiling point above the separated olefinic compound whereby said stable free radical in the feed stream being less than 700 parts per billion.

2. The method according to claim 1 wherein said stable free radical is a nitroxide having the formula:



wherein each of R_1 , R_2 and R_3 and R_4 is an alkyl group or heteroatom substituted alkyl group having 1 to 15 carbon atoms, R_5 and R_6 (a) each being an alkyl group having 1 to 15 carbon atoms, or a substituted alkyl group having 1 to 15 carbon atoms wherein the substituent is halogen, cyano, $-CONH_2$, $-SC_6H_5$, $-S-COCH_3$, $-OCOCH_3$, $-OCOC_2H_5$, carbonyl, or alkenyl wherein the double bond is not conjugated with the nitroxide moiety, $-COOR$ wherein R of the $-COOR$ group is alkyl or aryl, or (b) together forming part of a ring that contains 4 or 5 carbon atoms and up to two heteroatoms of O, N or S.

3. The method according to claim 2 wherein the R_1 , R_2 , R_3 and R_4 groups are each methyl, ethyl or propyl groups.

4. The method according to claim 3 wherein R_5 and R_6 are each methyl, ethyl or propyl groups.

5. The method according to claim 1 wherein the nitroxide is di-tert-butyl-nitroxide.
6. The method according to claim 2 wherein the nitroxide is a piperdino-1-oxyl, a pyrrolidino-1-oxyl or a pyrrolin-1-oxyl.
7. The method according to claim 6 wherein the nitroxide is 4-hydroxy-2,2,6,6-tetramethylpiperidino-1-oxy.
8. The method according to claim 6 wherein the nitroxide is 2,2,6,6-tetramethylpiperidino-1-oxy.
9. The method according to claim 6 wherein the nitroxide is 2,2,6,6-tetramethylpiperidino-1-oxy.
10. The method according to claim 2 wherein said nitroxide is 4-hydroxy-2,2,6,6-tetramethylpiperidino-1-oxy.
11. The method according to claim 1 wherein said stable free radical is produced in situ from a precursor.
12. The method according to claim 2 wherein said stable free radical is produced in situ from a precursor.
13. The method according to claim 2 wherein R_5 and R_6 together form part of a ring and wherein the ring structure formed by R_5 and R_6 contains a carbonyl.
14. The method as defined in claim 2 wherein the concentration of free radical in the bottoms liquid is less than 500 parts per billion.
15. The method as defined in claim 1 wherein the concentration of free radical in the bottoms liquid is less than 500 parts per billion.

16. The method as defined in claim 1 wherein the stable free radical is 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy and is present in the bottoms liquid at a concentration of less than 500 parts per billion.

17. The method of claim 2 wherein the nitroxide is present in the feed stream at a concentration of between about 20 to about 100 parts per billion.

18. The method as defined in claim 10 wherein the concentration of said nitroxide in the bottoms liquid is less than 500 parts per billion.

19. The process as defined in claim 1 wherein the hydrocarbon separated into an overhead stream is ethylene.



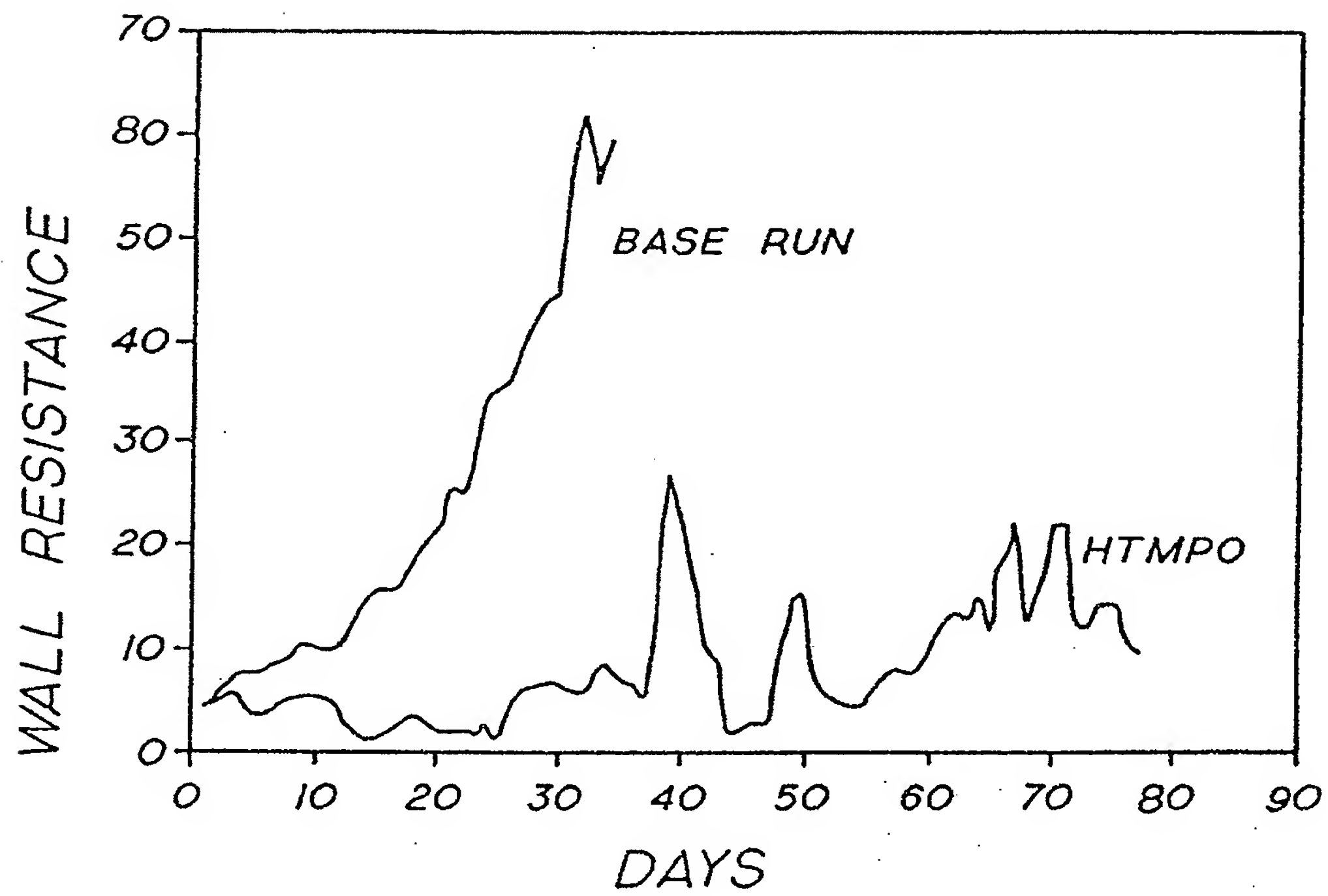


FIG. 1

Scott & Appleton